

Reciprocity law experiments in polymeric photodegradation: A critical review

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Reciprocity law experiments in polymeric photodegradation: a critical review

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Abstract

Accelerating the photodegradation of polymeric materials is of great practical interest in weathering research. Acceleration can be achieved by exposing polymeric materials to a high radiant flux; however, questions have arisen within the weathering community as to whether high radiant flux results can be extrapolated to in-service flux levels. Experiments designed to test this premise are called reciprocity law experiments. An extensive review has been conducted to assess the state-of-the-art of reciprocity law experiments in the photography, photoconductivity, photo-medicine, photobiology, and polymer photodegradation literatures. From this review, the Schwarzschild law (a power law generalization of the reciprocity law) appears to model adequately photoresponse vs. radiant flux for most materials and systems. A band theory model has been presented to explain variations in the Schwarzschild law coefficients and other experimental phenomena commonly associated with reciprocity experiments. Obstacles to the general acceptance of high radiant flux, laboratory-based experiments are discussed.

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1. Introduction

Polymeric materials exposed to solar ultraviolet (UV) radiation, heat, and moisture and other stress factors in both terrestrial and extra-terrestrial applications degrade through processes known collectively as weathering. Weathering can occur through these factors acting individually or in combination. For commercially viable materials, weathering is usually a slow process often taking 5 years or longer before a critical performance property of a material is said to have failed. Since performance data is required before a new product can enter the marketplace, the shortest time-to-market for a new polymeric product is essentially dictated by the time required in generating this data. A need exists, therefore, to develop exposure strategies that accelerate weathering while permitting valid extrapolations from accelerated stress levels to in-service exposure conditions.

For many polymeric materials, UV radiation plays the dominant, or at least a very important, role in weathering applications. This is especially true if the UV exposure occurs when the moisture content and temperature of the material are both high. At any given panel temperature and panel moisture content, the rate of weathering almost al-

ways increases with an increase in UV flux. Extrapolating high radiant flux results to low radiant flux levels has been successfully employed in the biological, medical, and the photoconductance industries over the last 100 years; while, in the materials weathering industry, this strategy has gained widespread acceptance in field exposure testing since the 1960s [30,46], but not in laboratory accelerated weathering experiments. The lack of acceptance in laboratory accelerated aging tests is due, in part, to the knowledge that the spectral emissions from laboratory light sources do not duplicate the solar spectrum and the belief that high radiant flux exposures may upset the balance of exposure conditions to which a laboratory specimen is exposed. This imbalance may result in polymeric materials failing through unnatural failure mechanisms, that is, failure mechanisms that cannot or do not occur outdoors [42,70].

The objectives of this paper are to review critically and assess the state-of-the-art of high radiant flux exposures and photodegradation of polymeric materials. This review covers a range of materials including those from the photographic, biological, medical, photoconductance, and photochemical communities. Specific objectives of this review include the following:

1. Describe the reciprocity law and its variations.
2. Present a variety of graphical techniques for assessing whether the reciprocity law is obeyed.

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3. Survey the photographic, medical, biological, photoconductive and polymeric materials reciprocity law literature and tabulate the observations.
4. Determine the percentage of cases in which the reciprocity law is obeyed; and, correspondingly, the percentage that it fails.
5. Analyze the tabulated data for patterns to ascertain whether high radiant flux experiments can be extrapolated back to in-service conditions, regardless whether the reciprocity law is obeyed.
6. Present a model, having a basis in solid state physics, that may universally describe photolytic processes and experimental phenomena commonly reported or observed in reciprocity experiments for all materials and systems.
7. Finally, identify future research needs.

Throughout this review, it is assumed that photophysical processes like photon absorption, localized excitation, and free carrier (excited electrons or holes) migration, are physical processes that are identical in all materials, while photochemical processes are more complex and often differ from material to material. These photophysical processes, however, are always a precursor of any photochemical change in a material. It is further assumed that only a fraction of the photoexcited electrons actually contribute to a photoreponse of a material; the remainder recombines releasing their energy through luminescence or heat generating processes.

1.1. Reciprocity law

Experiments in which the photoreponse of a material vary as a function of radiant flux are commonly called *reciprocity law experiments*. Bunsen and Roscoe [26] have been credited with conducting the first reciprocity law experiments. They concluded from their results that all photochemical reaction mechanisms depend only on the total absorbed energy and are statistically independent of the two factors that determine total absorbed energy, that is, radiant intensity, I , and exposure time, t . This hypothesis later became known as the reciprocity law because, in photography, the behavior of a series of photographic or radiographic films will be uniformly constant if the exposure times to which the films are exposed vary reciprocally with the intensities of the exposing radiation [133]. The reciprocity law has the form

$$It = \text{constant} \quad (1)$$

Experimental deviations from the reciprocity law are called *reciprocity law failure*.

Since the reciprocity law only depends on total absorbed energy, validation of the reciprocity law for a material can have many experimental manifestations (see Fig. 1). Assuming that the reciprocity law is valid, then each manifestation should be equivalent to the others as long as the integrated total absorbed energy is the same. Thus, when the reci-

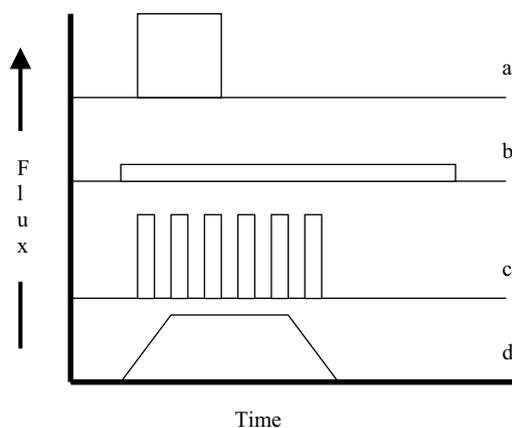


Fig. 1. A selection of radiant flux vs. exposure time regimes for testing the law of reciprocity in which the integrated area for each exposure regime are identical. When the reciprocity law is obeyed, the photoreponse for each of these exposure regimes is the same (adapted from [59]).

procity law is obeyed, the same photoreponse is observed when specimens receive the same integrated total absorbed energy or dosage regardless as to whether the exposures is performed:

- (a) At a high radiant flux for a short period of time.
- (b) At a low radiant flux for a long period of time.
- (c) By repeatably switching a light source on-or-off and controlling both the on-off frequency of the light and the length of time that the light remains in the on and the off state. Experiments in which the light is turned on-and-off at an extremely high frequency are called *flash photolysis experiments*; while experiments in which the light is turned on-and-off at a low frequency are called *intermittency experiments*.
- (d) By ramping the radiant flux to a high level, holding the flux for a specified period of time, and then ramping it back down to a lower level or any variant of these stress regimes.

These exposure regimes are graphically depicted in Fig. 1.

After Bunsen and Roscoe published their results, papers began to appear challenging the validity of the reciprocity law [1,2,3,55,164]. Reciprocity law failures were commonly observed for experiments conducted at either very low or very high radiant fluxes. To account for these failures, Schwarzschild [167], an astronomer, proposed a modification of the reciprocity law that fit his low intensity, stellar data. This empirical model later became known as *Schwarzschild's law* and is given by either

$$I^p t = \text{constant} \quad (2a)$$

or

$$It^p = \text{constant} \quad (2b)$$

where p is the Schwarzschild coefficient and is designated as the p -coefficient in this paper. Note that when $p = 1$,

Schwarzschild's and the reciprocity laws are identical and, hence, Schwarzschild's law is a generalization of the reciprocity law.

At the time that Schwarzschild published his paper, he thought that the p -coefficient was a constant having a value of 0.86. It quickly became apparent, however, that the value of the p -coefficient varied from material to material, varied within the same material (that is, it is not a material constant); and, in some cases, varied with a change in radiant flux.

Although the reciprocity law and Schwarzschild's law equations are the most common equations used in describing the photoresponse of a material as a function of radiant flux, other models and graphical techniques have been proposed (see [124,125] for an excellent review of these techniques). Few of these models and graphical techniques, however, have gained widespread acceptance either inside or outside the photographic field, the research discipline in which they were first proposed. The exception to this is the graphical technique popularized by Halm [81] that is based on Kron's [110] catenary equation

$$\log It = \text{constant} + \log \left[\left(\frac{I}{I_0} \right)^a + \left(\frac{I}{I_0} \right)^{-a} \right] \quad (3)$$

where I_0 and a are constants having values that vary from one photographic emulsion to another.

At low intensities, Eq. (3) reduces to

$$\log It = \text{constant} - a \log I \quad (4)$$

the above equation is used as the basis for Halm's $\log It$ vs. $\log I$ plots shown in Fig. 2 [124, p. 236]. When the $\log It$ vs. $\log I$ plot is linear and parallel to the abscissa, then the reciprocity law is obeyed. Correspondingly, when the $\log It$ vs. $\log I$ plot is non-linear (that is, when it has a catenary shape, the shape assumed by a string hanging freely between two horizontal supports), then reciprocity law failure is said to

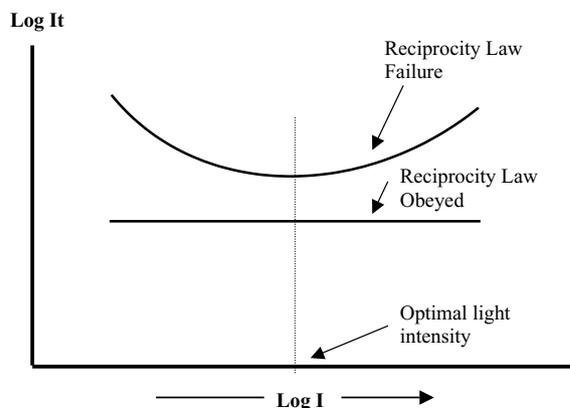


Fig. 2. Halm's graphical method for presenting reciprocity data in which the logarithm of dosage, $\log It$, necessary to produce a fixed photoresponse is plotted against the logarithm of radiant intensity (I). A line parallel to the abscissa indicates that the reciprocity law is obeyed. Otherwise, reciprocity failure is said to have occurred.

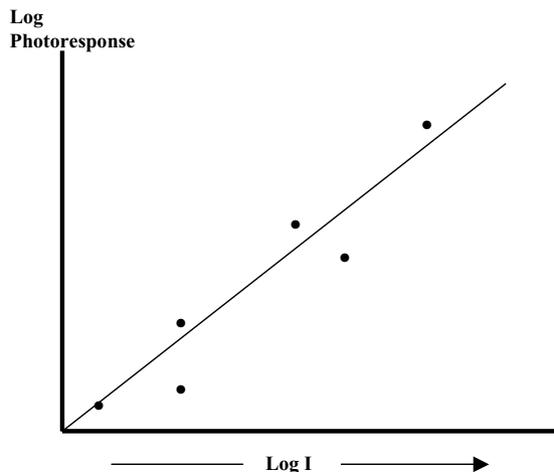


Fig. 3. Graphical technique commonly used in the non-photographic literature for assessing the validity of the reciprocity law.

have occurred. Although Eq. (3) is empirical in nature, it provides a good fit to almost all latent image experimental data. The optimal radiant flux level for a photographic emulsion is always the radiant flux at the lowest part of the $\log It$ vs. $\log I$ plot. This intensity level is often termed the optimal intensity or the intensity of maximum film sensitivity [133]. In practice, the $\log It$ vs. $\log I$ plot is only one of a family of plots relating dosage, It , exposure time, t , and radiant intensity, I . Other graphs include $\log It$ vs. $\log t$ and $\log I$ vs. $\log t$ plots. These plots are commonly used in establishing a relationship between the UV exposure environment and the photoresponse of a material and they can be modified to include the effect of temperature and moisture. Mees [124] should be consulted for details on the construction of these plots.

Outside the photographic field, the most common graphical presentation is a simple photoresponse vs. the logarithm of intensity plot based on Eq. (2) (see Fig. 3). This graph is constructed by plotting the logarithm of photoresponse vs. the logarithm of intensity [53,179,182]. If the data fall on the same line and if the slope of the line is 1, then the reciprocity law is obeyed. If the data fall on the same line, but the slope of the line is not equal to 1, then the Schwarzschild law is obeyed and the p -coefficient is the slope of the line. Finally, if the data do not fall on the same line, then the Schwarzschild p -coefficient varies within a material and the value of the coefficient depends on the radiant flux.

1.2. Literature survey

From 1880 through the early part of the 20th century, the majority of reciprocity law experiments were performed on photographic materials. At the turn of the 20th century, however, the medical profession independently began to validate the reciprocity law for erythema (reddening of the skin) and phototherapy (the use of high UV radiant fluxes to cure diseases like tuberculosis and rickets). In the 1930s, these medical studies were extended to biological applications

including the purification of water and the determination of the biocidal efficiencies of different spectral wavebands and different light sources in deactivating viruses, bacteria, fungi, and mold. With the discovery of xerography (or more precisely electrophotographic printing) in the 1940s, the emphasis of reciprocity law research rapidly shifted to photoconductance studies. These photoconductance studies were later extended to photovoltaic cells and the photodecomposition of a wide variety of hazardous chemicals via photocatalytic oxidation of semiconductors [130]. Photoconductance and photocatalytic studies continue to dominate the reciprocity law literature. In comparison, high radiant flux laboratory-based experiments for weathering polymeric ma-

terials have been disjunctively investigated and have never nucleated concerted, methodical investigations to unravel dose–response effects at a fundamental photochemical or photophysical level.

This review chronologically tracks the history of reciprocity experimentation; that is, the order of presentation is: (1) photography, (2) photo-medicine and photobiology, (3) photoconductance, and, finally, (4) the photodegradation of polymeric materials. Within each discipline, data are catalogued by publication date and include information on the author(s), exposed material, material photoresponse, light source, wavelength, type of exposure regime (i.e., continuous or intermittent), and, finally, the Schwarzschild

Table 1
Reciprocity experimental data—photographic darkening^a

References	Material	Response	Light source (flux factor)	Mono/polychromatic	Continuous/intermittent	<i>p</i> -Coefficient
[26]	Variety of chemicals	Darkening	Amyl acetate (?)	?	?	1
[2]	Emulsion	Darkening	Amyl acetate (?)	Polychromatic	Continuous	rf
[3]	Emulsion	Darkening	Multiple (576)	Polychromatic	Continuous	rf
[165]	Emulsion	Darkening	Starlight (?)	Polychromatic	Continuous	1
[164]	Emulsion	Darkening	Starlight (?)	Polychromatic	Continuous	rf
[148]	Emulsion	Darkening	X-ray (?)	Polychromatic	Continuous	1
[167]	Emulsion	Darkening	Oil lamp (10 ³)	Polychromatic	Continuous	0.86
[184]	Emulsion #1	Darkening	Acetylene (36)	Polychromatic	Continuous	0.84
[184]	Emulsion #2	Darkening	Acetylene (36)	Polychromatic	Continuous	0.83
[111]	Emulsion	Darkening	X-ray (4)	Monochromatic	Continuous	1
[67]	Emulsion	Darkening	X-ray (100)	?	?	rf
[72]	Emulsion	Darkening	X-ray (7)	Polychromatic	?	1
[86]	Emulsion	Darkening	? (250)	Monochromatic	Continuous	1
[87]	Emulsion	Darkening	? (250)	Monochromatic	Continuous	1
[23]	Emulsion	Darkening	X-ray (10)	Polychromatic	Continuous	1
[98]	Emulsion #1	Darkening	Incandescent (10 ⁵)	Polychromatic	Continuous	0.63–1.07
[98]	Emulsion #2	Darkening	Incandescent (10 ⁶)	Polychromatic	Continuous	1
[98]	Emulsion #3	Darkening	Incandescent (10 ⁶)	Polychromatic	Continuous	0.68–1.0
[79]	Emulsion	Darkening	Mercury (5)	Polychromatic	Continuous	1
[99]	Emulsion #1	Darkening	Incandescent (10 ⁷)	Polychromatic	Continuous	1
[99]	Emulsion #2	Darkening	Incandescent (10 ⁷)	Polychromatic	Continuous	1
[99]	Emulsion #3	Darkening	Incandescent (10 ⁷)	Polychromatic	Continuous	1
[82]	Emulsion	Darkening	Incandescent (500)	Polychromatic	Continuous	1
[54]	Emulsion	Darkening	? (10 ⁹)	?	Continuous	0.04–1.85
[140]	Emulsion	Darkening	Mercury (?)	Polychromatic	Continuous	rf
[92]	Emulsion	Darkening	Gamma (10 ⁴)	Polychromatic	Continuous	1
[51]	Emulsion	Darkening	X-ray (20)	Monochromatic	Continuous	1
[185]	Emulsion #1	Darkening	Mercury (10 ⁵)	Monochromatic	Continuous	rf
[185]	Emulsion #2	Darkening	Mercury (10 ⁵)	Monochromatic	Continuous	rf
[186]	Emulsion #1	Darkening	Mercury (10 ⁵)	Monochromatic	Continuous	rf
[186]	Emulsion #1	Darkening	Mercury (10 ⁵)	Monochromatic	Intermittent	rf
[186]	Emulsion #2	Darkening	Mercury (10 ⁵)	Monochromatic	Continuous	rf
[186]	Emulsion #2	Darkening	Mercury (10 ⁵)	Monochromatic	Intermittent	rf
[186]	Emulsion #3	Darkening	Mercury (10 ⁵)	Monochromatic	Continuous	rf
[186]	Emulsion #3	Darkening	Mercury (10 ⁵)	Monochromatic	Intermittent	rf
[186]	Emulsion #4	Darkening	Mercury (10 ⁵)	Monochromatic	Continuous	rf
[186]	Emulsion #4	Darkening	Mercury (10 ⁵)	Monochromatic	Intermittent	rf
[159]	Emulsion	Darkening	Gamma (10 ⁴)	Polychromatic	Continuous	1
[159]	Emulsion	Darkening	Gamma (10 ⁴)	Polychromatic	Intermittent	1
[14]	Emulsion #1	Darkening	X-ray (10 ⁴)	Polychromatic	Continuous	1
[14]	Emulsion #2	Darkening	X-ray (10 ⁴)	Polychromatic	Intermittent	1
[133]	Emulsion #1	Darkening	X-ray (10 ⁴)	?	Continuous	1
[133]	Emulsion #2	Darkening	X-ray (10 ⁴)	?	Continuous	rf

^a The symbol ‘?’ indicates that the author did not provide this information in his (her) publication.

p -coefficient. Also included in brackets in the “light source column” is the experimental radiant flux factor over which the reciprocity law was evaluated. In many cases, the author(s) did not provide all of the desired information; the absence of such data is indicated by “?”. Also, in many cases the author(s) did not compute the Schwarzschild p -coefficient, but, instead, only indicated that the reciprocity law failure occurred which is indicated by the letters ‘rf’.

In making comparisons within and between disciplines, several practical experimental considerations should be kept in mind. First, prior to about 1970, light source feedback-control devices for controlling the radiant flux intensity of a light source were not readily available and, thus, the contribution to the total variation from changes in the radiant flux intensity are unknown but may be large. Other sources of experimental errors include the accuracy and precision of the photoresponse measurements. In many of the disciplines, photoresponse is qualitatively assessed using criteria like reddening of the skin, tumor formation, and fading of paints. The magnitude of the measurement error for these measurements is unknown. Finally, very few of the experiments included specimen replication making it impossible to estimate confidence bands for the reported p -coefficient values.

1.3. Photographic darkening

Photographic emulsions are essentially semiconductor particles (silver halide) dispersed in a polymeric (gelatin) matrix. Pigmented or filled commercial polymeric materials are essentially semiconductor particles (e.g., colorants,

titanium dioxide and zinc oxide) dispersed in a polymeric matrix. The major difference between the two systems is in the absorption bands of the particles. Silver halide pigments absorb in the visible region whereas titanium dioxide and zinc oxide absorb in the UV. In the photographic literature, it is generally recognized that the pigment, as opposed to the resin matrix material, is the primary chromophore, and increasing evidence exists that the pigment may also be the primary chromophore in the photodegradation of coatings and other pigmented construction materials [52,73]. Thus, data for photographic emulsions may provide valuable insight into the photoresponse of pigmented commercial polymeric systems.

Of all the disciplines that were reviewed, the photographic literature includes the largest number of reciprocity law experiments before the 1940s. As such, most of these studies were conducted prior to the advent of computers. In the absence of computers, the photographic community employed graphical $\log It$ vs. $\log I$ plots in presenting its data as opposed to determining the Schwarzschild coefficient. For this reason, the photographic citations account for the largest proportion of “rf” (reciprocity failure) observations (the percentage of rf vs. total number of observations is 36% for photography, 15% for medical, 2% for biological, 0% for photoconductance, and 17% for materials weathering). With this in mind, the photographic darkening data are tabulated in Table 1.

The distribution of p -coefficient values for photographic darkening is presented in Fig. 4. In constructing this figure, the data from Eggert and Arens [54] were not included in the histogram, since we were not able to locate the original paper

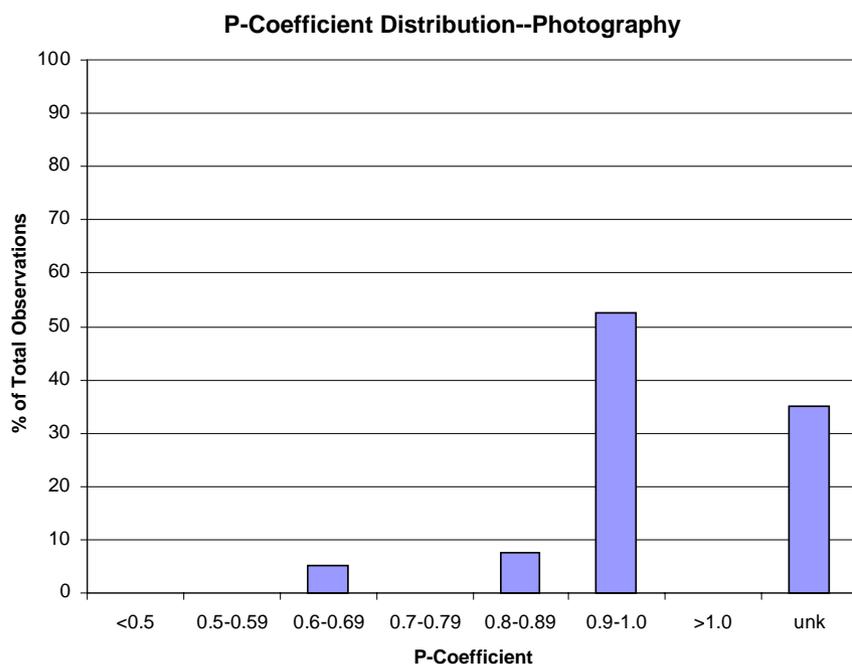


Fig. 4. Distribution of Schwarzschild p -coefficients for the darkening of photographic emulsions. The category ‘unk’ indicates that reciprocity failure was observed, but the p -coefficient was not computed.

(i.e., the values reported in the table were reported in another paper) and it was not known how these values were obtained or how many emulsions were investigated. From Fig. 4, the reciprocity law was obeyed in greater than half of the observations and all of the p -coefficient estimates that were not designated as “rf” fell in the range between 0.6 and 1.1.

1.4. Biological and medical

Reciprocity law experiments in the biological and medical disciplines involve the absorption and interaction of UV,

X-ray, or gamma radiation with complex, natural polymers. Biological and medical materials, like synthetic polymers, are carbon-based molecules that degrade through photooxidation processes that are similar to those causing the photooxidation of synthetic polymers. These natural molecules differ from synthetic polymers mainly in their complexity and, if given enough time, their ability to heal or regenerate when they are in a living system. Thus, the response of natural polymers to high radiant fluxes is pertinent to the reciprocity law literature for the photoresponse of synthetic materials.

Table 2
Reciprocity experimental data—biological materials

References	Material	Response	Light source (flux factor)	Mono/polychromatic	Continuous/intermittent	p -Coefficient
[24]	Amoebae	Inactivation	Hydrogen discharge (10)	Polychromatic	Intermittent	1
[89]	Protozoan	Inactivation	Mercury (9)	Polychromatic	Continuous	1
[38]	Bacteria	Inactivation	Mercury (125)	Polychromatic	Continuous	rf
[38]	Bacteria	Inactivation	Mercury (?)	Polychromatic	Intermittent	1
[132]	Bacteria	Inactivation	? (?)	?	?	1
[68]	Bacteria	Inactivation	Mercury (4)	Monochromatic	Continuous	1.1
[69]	Bacteria	Inactivation	Mercury (4)	Monochromatic	Continuous	1.1
[193]	Paramecium	Inactivation	Mercury (4)	Monochromatic	Continuous	1
[174]	Protozoan	Inactivation	Mercury (8)	Monochromatic	Continuous	1
[9]	Bacteria	Inactivation	? (10^5)	?	?	1
[177]	Drosophila (fruit fly)	mutation	X-ray (30)	Monochromatic	Continuous	1
[31]	Drosophila	Mutation	X-ray (20)	?	Continuous	1
[107]	Bacteria	Inactivation	Mercury (1500)	Polychromatic	Continuous	1
[107]	Mold	Inactivation	Mercury (1500)	Polychromatic	Continuous	1
[151]	Drosophila	Mutation	Gamma (800)	Polychromatic	Continuous	1
[178]	Drosophila	Mutation	X-ray (300)	?	Continuous	1
[114]	Bacteria	Inactivation	Mercury (500)	Monochromatic	Continuous	1
[114]	Virus	Inactivation	X-ray (3)	Monochromatic	Continuous	1
[114]	Virus	Inactivation	Mercury (120)	Monochromatic	Continuous	1
[134]	Drosophila	Mutation	X-ray (5000)	?	Continuous	1
[153]	Paramecium	Inactivation	Mercury (10^7)	Polychromatic	Flash	1
[154]	Bacteria	Inactivation	Mercury (10^5)	Polychromatic	Flash	1
[113]	Yeast	Inactivation	? (?)	?	?	1
[58]	Bacteria	Inactivation	Mercury (25)	Monochromatic	?	1
[102,103]	Bacteria	Photorecovery	Incandescent (?)	Polychromatic	Continuous	1
[123]	Protein	Inactivation	Mercury (6)	Monochromatic	Continuous	1
[27]	Bacteria #1	Inactivation	Mercury (10^8)	?	Continuous	1
[27]	Bacteria #2	Inactivation	Mercury (10^8)	?	Continuous	1
[27]	Fungus	Inactivation	Mercury (10^8)	?	Continuous	1
[34]	Protozoan	Inactivation	Mercury (3)	Monochromatic	Continuous	1
[117]	Bacteria	Inactivation	Mercury (10^5)	Monochromatic	Continuous	1
[71]	Protozoan	Inactivation	Mercury (3)	Monochromatic	Intermittent	1
[104]	Yeast	Mutation	Mercury (126)	Monochromatic	Flash	1
[106]	Pollen	Mutation	Mercury (10)	Monochromatic	Continuous	1
[199]	Fungus	Inactivation	Mercury (?)	Polychromatic	Intermittent	1
[199]	Fungus	Inactivation	Mercury (?)	Polychromatic	Continuous	1
[112]	Mustard seed	Chemical production	? (100)	Monochromatic	Continuous	1
[194]	Parsley	Chemical production	? (9)	Monochromatic	Continuous	1
[146]	Bacteria #1	Inactivation	Mercury (2)	Monochromatic	Continuous	1
[146]	Bacteria #2	Inactivation	Mercury (4)	Monochromatic	Continuous	1
[149]	Alfalfa seedling	Mutation	Fluorescent (10)	Polychromatic	Continuous	1
[173]	Alfalfa seedling	Mutation	Mercury (4)	Monochromatic	Continuous	1
[190]	Bacteria	Inactivation	Fluorescent (10)	Polychromatic	Continuous	1
[93]	Bacteria	Inactivation	Fluorescent (10)	Polychromatic	Continuous	1
[93]	Yeast	Inactivation	Mercury (10)	Polychromatic	Continuous	1
[94]	Bacteria	Inactivation	Fluorescent (14)	Polychromatic	Continuous	1

Table 3
Reciprocity experimental data—medical

References	Material	Response	Light source (flux factor)	Mono/polychromatic	Continuous/intermittent	<i>p</i> -Coefficient
[83]	Human skin	Erythema	Mercury (4)	Monochromatic	Continuous	1
[84]	Human skin	Erythema	Mercury (?)	Monochromatic	Continuous	1
[163]	Human skin	Erythema	? (?)	?	?	rf
[118]	Ergosterol	Vitamin D production	Cadmium (100)	Monochromatic	Continuous	1
[116]	Human skin	Erythema	Mercury (8)	?	Continuous	1
[116]	Human skin	Rickets	Mercury (?)	?	Continuous	1
[39]	Human skin	Erythema	Mercury (4)	Monochromatic	Continuous	1
[16]	Mice	Tumorogenesis	Mercury (12)	Polychromatic	Continuous	1
[17]	Mice	Tumorogenesis	Mercury (4)	Polychromatic	Intermittent	1
[10]	Mice	Tumorogenesis	Mercury (4)	Polychromatic	Intermittent	rf
[18]	Human skin	Erythema	Carbon (?)	Polychromatic	Continuous	1.2
[18]	Human skin	Erythema	Mercury (20)	Monochromatic	Continuous	1
[35]	Mice	Tissue damage	Mercury (10 ⁷)	Monochromatic	Flash	1
[36]	Mice	Tissue damage	Mercury (10 ⁸)	Monochromatic	Flash	1
[166]	Human skin	Erythema	Mercury (200)	Monochromatic	Flash	1
[57]	Human skin	Erythema	Xenon (?)	Monochromatic	Intermittent	1
[57]	Human skin	Erythema	Xenon (?)	Monochromatic	Continuous	1
[145]	Human skin	Erythema	Laser (3)	Monochromatic	Flash	1
[59]	Mice	Tumorogenesis	Xenon (3)	Monochromatic	Intermittent	rf
[47]	Mice	Immunosuppression	Fluorescent (1)	Polychromatic	Intermittent	1
[48]	Mice	Immunosuppression	Fluorescent (10)	Polychromatic	Continuous	1
[5]	Human skin	Erythema	Laser (10 ⁴)	Monochromatic	Continuous	1
[60]	Mice	Tumorogenesis	Fluorescent (5)	Polychromatic	Continuous	rf
[138]	Mice	Immunosuppression	Fluorescent (10)	Polychromatic	Continuous	1
[49]	Mice	Tumorogenesis	Fluorescent (8)	Polychromatic	Continuous	1
[144]	Human skin	Erythema	Mercury (10 ³)	Monochromatic	Continuous	1

The division between biological and medical is arbitrary. In this review, biological applications include the inactivation of viruses, bacteria, fungi, mold, and algae whereas medical applications include erythema, tumorogenesis, skin cancer, and the curing of diseases like tuberculosis and rickets. The biological data are presented in Table 2, and the medical data are presented in Table 3.

The distributions of *p*-coefficients for biological and medical applications are displayed in Figs. 5 and 6, respectively. Unlike the results for photography, the reciprocity law was obeyed in the overwhelming majority of the biological and medical applications. Three *p*-coefficient values, two in the biological literature and one in the medical literature, had values slightly greater than 1.0. It was not possible to as-

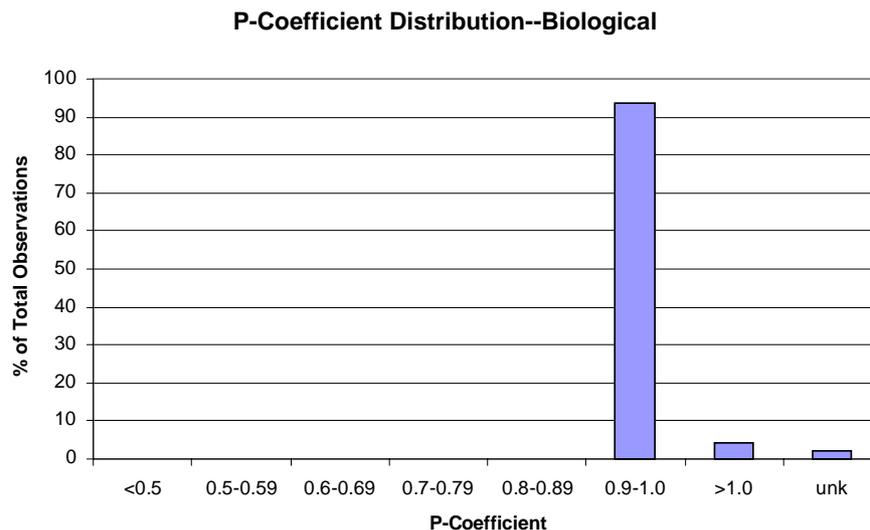


Fig. 5. Distribution of Schwarzschild *p*-coefficients for biological materials. The category 'unk' indicates that reciprocity failure was observed, but the *p*-coefficient was not computed.

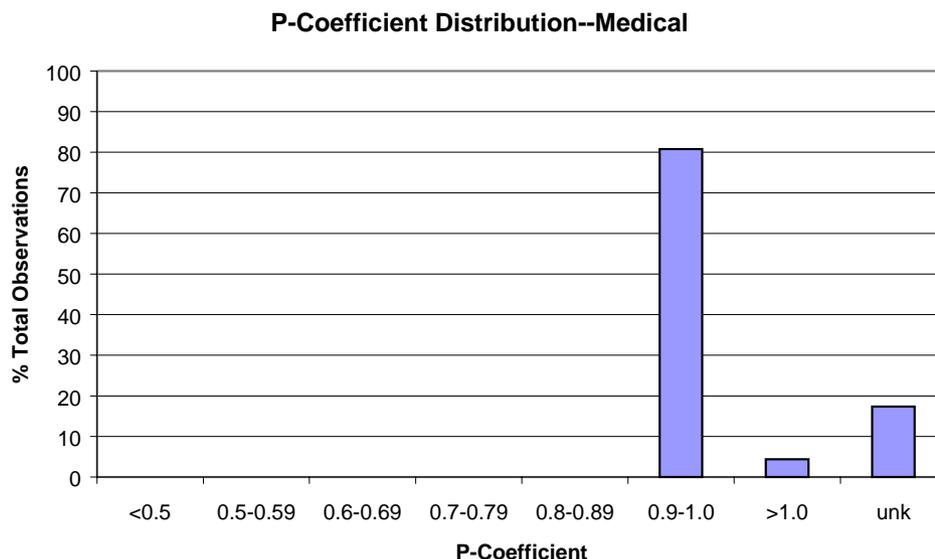


Fig. 6. Distribution of Schwarzschild p -coefficients for medical applications. The category 'unk' indicates that reciprocity failure was observed, but the p -coefficient was not computed.

certain whether these p -coefficient values are significantly greater than 1, because the authors did not provide any information on data scatter. From the tables, two of the three p -coefficients were published in 1929 and the third in 1946. All three observations, therefore, were made prior to the advent of light source radiant flux feedback-control systems and, thus, these p -coefficient values may not be significantly different from 1.

1.5. Photoconductance (photovoltaic, photoelectrochemical)

All materials (crystalline, semi-crystalline, amorphous, organic, and inorganic) photoconduct when exposed to radiation having sufficient energy to excite an electron into the material's conduction band [76,77,127]. Becquerel [13] observed the photoelectrochemical effect when he connected a silver chloride electrode to a counter electrode and immersed the electrodes in a sunlight-irradiated electrolyte. Smith [171] is credited as being the first to observe material photoconductance when he irradiated selenium with sunlight. Although the photoconductance phenomenon was discovered in the 19th century, the science of photoconductance had to wait until the turn of the 20th century until electronic equipment sensitive enough to measure high electrical resistances became available [108]. Interest in the photoconducting properties of materials rapidly increased during the 1950s with the advent of electrophotographic printing [196], during the 1970s with increased demands for efficient solar energy photovoltaic cells, and during the 1990s with environmental demands to mineralize hazardous chemicals. Photoconductance data are tabulated in Table 4.

The distribution of the p -coefficients for photoconductance is displayed in Fig. 7. The plurality of observations,

specifically 43%, obeys the reciprocity law. Approximately 97% of the observations fall in the range $0.5 \leq p \leq 1.0$. There are two noteworthy exceptions. One observation has a value less than 0.5 while the other has a value greater than 1.0; both observations were made by the same author on the same material and this material is of critical importance in the weathering of polymeric construction materials—titanium dioxide, TiO_2 . Vohl's [182] p -coefficient value is significantly greater than 1. Rose [155] provides an explanation for p -coefficient values greater than 1 through a process called *supralinearity*. The reader should note that although the majority of the light sources in Table 4 were high-energy sources, photoconductivity in polymeric materials has been observed when polymeric materials have been exposed to incandescent radiation [8,97] and UV radiation from other light sources [8,180]. Indeed, the majority of modern day photoreceptors in electrophotographic printing systems are polymeric [21,22]. Thus, these observations provide strong support for the assumption that the photon absorption, electron excitation, and free carrier (excited electrons and holes) migration processes apply to polymeric materials (see [77, Chapters 16 and 18]).

1.6. Photodegradation of materials

All polymeric materials photodegrade when exposed outdoors to solar radiation. Reciprocity experiments have been conducted on only a few polymeric systems and, as in the photoconductance literature, seldom does more than one researcher investigate the same polymer and seldom are the investigated polymers neat polymers; instead, the polymers investigated were usually commercial grade. Moreover, almost all of the photodegradation of materials reciprocity experiments performed that have been conducted have been

Table 4
Reciprocity experimental data—photoconductance

References	Material	Response	Light source (flux factor)	Mono/polychromatic	Continuous/intermittent	p -Coefficient
[74]	Zinc blend	Photoconductance	? (3)	?	Continuous	1
[74]	HgS	Photoconductance	? (3)	?	Continuous	1
[183]	Stibnite	Photoconductance	? (30)	Monochromatic	Continuous	1
[61]	Antimony trisulfide	Photoconductance	? (100)	Monochromatic	Continuous	0.7
[170]	Cadmium sulfide	Photoconductance	Mercury (1000)	Polychromatic	Continuous	0.92
[170]	Cadmium sulfide	Photoconductance	Mercury (100)	Polychromatic	Continuous	0.58
[191]	Amorphous selenium	Photoconductance	? (?)	Polychromatic	Continuous	0.9
[191]	Amorphous selenium	Photoconductance	? (?)	Polychromatic	Continuous	0.5
[121]	Polyethylene	Photoconductance	Gamma (100)	Polychromatic	Continuous	0.75
[63]	Poly(tetra-fluoro-ethylene)	Photoconductance	X-ray (30)	Polychromatic	Continuous	0.63
[64]	Polyene	Photoconductance	X-ray (400)	Polychromatic	Continuous	0.8
[64]	Amber	Photoconductance	X-ray (60)	Polychromatic	Continuous	1
[65]	Polystyrene	Photoconductance	X-ray (32)	Polychromatic	Continuous	0.6
[40]	Polystyrene	Photoconductance	Beta particles (?)	Polychromatic	Continuous	0.75
[40]	Corning Vycor	Photoconductance	Beta particles (?)	Polychromatic	Continuous	0.85
[40]	Mica	Photoconductance	Beta particles (?)	Polychromatic	Continuous	1
[40]	Poly(methyl methacrylate)	Photoconductance	Beta particles (?)	Polychromatic	Continuous	1
[40]	Kel-F	Photoconductance	Beta particles (?)	Polychromatic	Continuous	0.75
[40]	Polyethylene	Photoconductance	Beta particles (?)	Polychromatic	Continuous	0.75
[62]	Polyethylene cable	Photoconductance	X-ray (10^4)	Polychromatic	Continuous	0.81
[62]	Polyethylene film	Photoconductance	X-ray (10^4)	Polychromatic	Continuous	0.82
[62]	Polyethylene	Photoconductance	X-ray (10^4)	Polychromatic	Continuous	0.79
[62]	Molded amber	Photoconductance	X-ray (10^4)	Polychromatic	Continuous	1
[62]	Natural amber	Photoconductance	X-ray (10^4)	Polychromatic	Continuous	1
[62]	Plasticized poly(methyl methacrylate)	Photoconductance	X-ray (10^4)	Polychromatic	Continuous	1
[62]	Mica	Photoconductance	X-ray (10^4)	Polychromatic	Continuous	0.95
[62]	Poly(methyl methacrylate)	Photoconductance	X-ray (10^4)	Polychromatic	Continuous	0.93
[62]	Poly(ethylene terephthalate)	Photoconductance	X-ray (10^4)	Polychromatic	Continuous	0.83
[62]	Polystyrene	Photoconductance	X-ray (10^4)	Polychromatic	Continuous	0.75
[62]	Polystyrene	Photoconductance	X-ray (10^4)	Polychromatic	Continuous	0.65
[62]	Poly(tetra-fluoro-ethylene)	Photoconductance	X-ray (10^4)	Polychromatic	Continuous	0.63
[62]	Poly(methyl methacrylate)	Photoconductance	X-ray (10^4)	Polychromatic	Continuous	0.55
[8]	Copper phthalocyanine	Photoconductance	Incandescent (100)	Polychromatic	Continuous	0.5
[8]	Copper phthalocyanine	Photoconductance	Mercury (100)	Polychromatic	Continuous	0.5
[8]	Copper phthalocyanine	Photoconductance	Sodium (100)	Polychromatic	Continuous	0.5
[25]	Cadmium sulfide #1	Photoconductance	Incandescent (?)	Polychromatic	Continuous	1
[25]	Cadmium sulfide #2	Photoconductance	Incandescent (?)	Polychromatic	Continuous	0.5
[128]	Zinc oxide	Photoconductance	? (10^3)	?	Continuous	1
[41]	Anthracene III	Photoconductance	Mercury (10^3)	Polychromatic	Continuous	0.95–1.05
[41]	Anthracene III	Photoconductance	Mercury (10^3)	Polychromatic	Continuous	0.5–0.6
[19]	9,10-Dichloro-anthracene	Photoconductance	? (12)	Polychromatic	Continuous	0.7
[157]	B-carotene	Photoconductance	Incandescent (?)	Polychromatic	Continuous	1
[179]	Phthalocyanine	Photoconductance	Xenon (10^3)	?	Continuous	0.57
[179]	Pyranthrene	Photoconductance	Xenon (10^3)	?	Continuous	0.63
[160]	Perylene crystal	Photoconductance	Incandescent (12)	Polychromatic	Continuous	0.68
[160]	Phthalocyanine	Photoconductance	Incandescent (12)	Polychromatic	Continuous	1
[160]	Merocyanine	Photoconductance	Incandescent (12)	Polychromatic	Continuous	1
[126]	Merocyanine	Photoconductance	? (6)	?	?	1
[122]	Paraffin	Photoconductance	X-ray (30)	Polychromatic	Continuous	0.72
[66]	<i>n</i> -Hexane (in solution)	Photoconductance	Gamma (10^3)	Polychromatic	Continuous	0.8
[66]	<i>n</i> -Hexane (liquid)	Photoconductance	Gamma (10^3)	Polychromatic	Continuous	0.51
[66]	Paraffin	Photoconductance	Gamma (10^2)	Polychromatic	Continuous	0.5
[66]	<i>n</i> -Hexane (solid)	Photoconductance	Gamma (10^3)	Polychromatic	Continuous	0.5
[180]	Poly-Schiff type polymer	Photoconductance	Mercury (?)	Monochromatic	Continuous	0.55
[180]	Polyazine type polymer	Photoconductance	Mercury (?)	Monochromatic	Continuous	0.8
[97]	Fluoridine	Photoconductance	Incandescent (100)	Polychromatic	Continuous	1
[97]	Triphenodioxane	Photoconductance	Incandescent (100)	Polychromatic	Continuous	1
[127]	Cadmium sulfide	Photoconductance	? (6)	?	Continuous	1
[182]	Titanium dioxide film	Photoconductance	? (?)	Monochromatic	Continuous	1.6
[182]	Titanium dioxide film	Photoconductance	? (?)	Monochromatic	Continuous	0.4
[162]	Polyvinyl carbazole type polymer	Photoconductance	? (30)	Polychromatic	Continuous	0.75
[37]	doped TiO ₂	Photoconductance	Xenon (100)	Monochromatic	Continuous	1

Table 4 (Continued)

References	Material	Response	Light source (flux factor)	Mono/polychromatic	Continuous/intermittent	<i>p</i> -Coefficient
[129]	C ₆₀ film	Photoconductance	Laser (6)	Monochromatic	Continuous	1
[136]	TiO ₂ doped film	Photoconductance	Xenon (4)	Polychromatic	Continuous	1
[120]	TiO ₂ film	Photoconductance	Laser (40)	Monochromatic	Continuous	1
[120]	TiO ₂ film	Photoconductance	Laser (40)	Monochromatic	Continuous	0.5
[197]	Photovoltaic cell	Photoconductance	? (10 ⁵)	Monochromatic	Continuous	0.94

performed as a “side experiment” in the context of a much larger study. No reciprocity experiment studies were found in the literature in which fundamental photophysical or photochemical events were systematically studied.

Since the late 1970s, extensive experimental efforts have been undertaken to determine the photocatalytic activity of pigments such as titanium dioxide, TiO₂, and zinc oxide, ZnO, at high radiant fluxes. In these experiments, pigments

are mixed into a solvent (often an alcohol), the mixture is irradiated, and the oxidation of this solvent is observed. Although not a perfect fit, these experimental results (indicated in the column marked materials by “+TiO₂” or “+ZnO”) have been included in Table 5.

The distribution of *p*-coefficients for the photodegradation of polymeric materials is displayed in Fig. 8. In the majority of the cases, the reciprocity law was obeyed. One

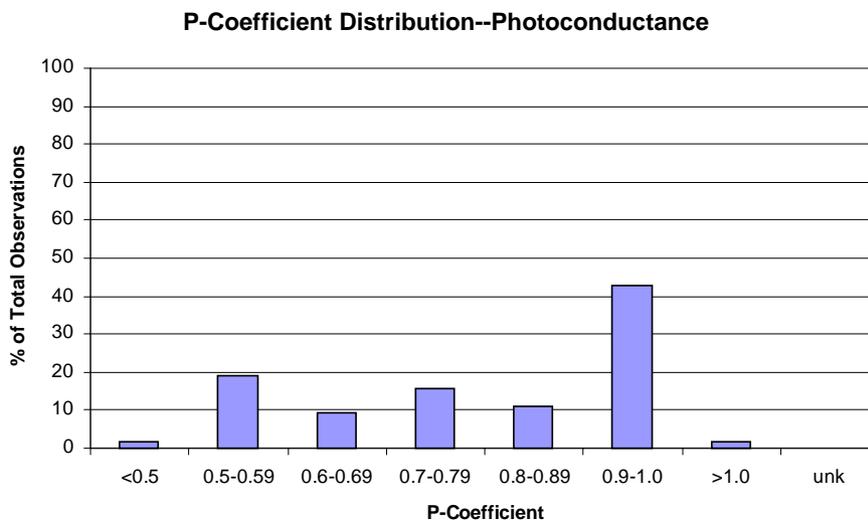


Fig. 7. Distribution of Schwarzschild *p*-coefficients for photoconductance. The category ‘unk’ indicates that reciprocity failure was observed, but the *p*-coefficient was not computed.

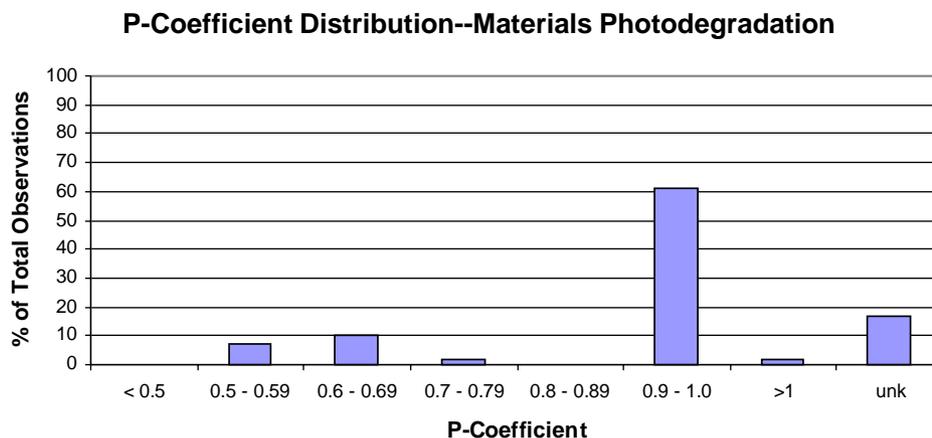


Fig. 8. Distribution of Schwarzschild *p*-coefficients for material photodegradation. The category ‘unk’ indicates that reciprocity failure was observed, but the *p*-coefficient was not computed.

Table 5
Reciprocity experimental data—photodegradation of materials

References	Material	Response	Light source (flux factor)	Mono/polychromatic	Continuous/intermittent	<i>p</i> -Coefficient
[115]	Textiles	Color change	Incandescent (54)	Polychromatic	Continuous	1
[95]	Methylene blue	Fading	Mercury (?)	Polychromatic	Continuous	1
[95]	Methyl violet	Fading	Mercury (?)	Polychromatic	Continuous	rf
[95]	Rhodamine	Fading	Mercury (?)	Polychromatic	Continuous	rf
[189]	Asphalt	Photodegradation	Carbon arc (?)	Polychromatic	Continuous	1
[32]	Polystyrene	Viscosity	Mercury (28)	Polychromatic	Continuous	1
[105]	Acetaldehyde	Photodegradation	Hydrogen krypton (70)	Polychromatic	Flash	1
[172]	Poly- α -methylstyrene	viscosity	Mercury (20)	Polychromatic	Continuous	1
[141]	Polyethylene	Gel content	X-ray (12)	Polychromatic	Continuous	1
[141]	Polyethylene	Swelling	X-ray (10)	Polychromatic	Continuous	1
[195]	Asphalt	Photodegradation	Carbon arc (2)	Polychromatic	Continuous	1
[142]	Coating #1	Solar absorbance	Mercury (10)	Polychromatic	Continuous	1
[142]	Coating #2	Solar absorbance	Mercury (10)	Polychromatic	Continuous	1
[142]	Coating #3	Solar absorbance	Mercury (10)	Polychromatic	Continuous	1
[142]	Coating #4	Solar absorbance	Mercury (10)	Polychromatic	Continuous	1
[142]	Coating #5	Solar absorbance	Mercury (10)	Polychromatic	Continuous	1
[198]	Coating	Solar reflectance	Mercury (2)	Polychromatic	Continuous	rf
[143]	Phenol + ZnO	Photocatalytic oxidation	Mercury (?)	Polychromatic	Continuous	1
[152]	Poly(vinyl chloride)	Photodegradation	Mercury (2)	Polychromatic	Continuous	rf
[161]	Poly(vinyl chloride)	Photodegradation	Xenon (3)	Polychromatic	Continuous	1
[90]	Coatings	Gloss loss	Xenon (4)	Polychromatic	Continuous	rf
[91]	Coatings	Chalking	Xenon (4)	Polychromatic	Continuous	rf
[44]	ABS terpolymer	Photodegradation	Fluorescent (6)	Polychromatic	Continuous	1
[45]	Polysulfone	Chemical change	Xenon (6)	Polychromatic	Continuous	1
[43]	Isopropanol + TiO ₂	Photocatalytic oxidation	Mercury (10)	Polychromatic	Continuous	1
[53]	Isopropanol + TiO ₂	Photocatalytic oxidation	Xenon (10 ³)	Polychromatic	Continuous	1
[53]	Isopropanol + TiO ₂	Photocatalytic oxidation	Xenon (10 ⁴)	Polychromatic	Continuous	0.5
[147]	PPO	Color change	Fluorescent (20)	Polychromatic	Continuous	rf
[109]	Chloroform + TiO ₂	Photocatalytic oxidation	Xenon (20)	Polychromatic	Continuous	0.5
[181]	Asphalt	Photooxidation	Xenon (55)	Polychromatic	Continuous	1
[200]	Trichloro-ethylene + TiO ₂	Photocatalytic oxidation	Solar (?)	Polychromatic	Continuous	0.65
[139]	Toluene + TiO ₂	Photocatalytic oxidation	Mercury and xenon (?)	Polychromatic	Continuous	0.55
[28]	Phenol + TiO ₂	Photocatalytic oxidation	Xenon (?)	Polychromatic	Continuous	0.68
[96]	Hydrogen peroxide + TiO ₂	Photocatalytic oxidation	Mercury (32)	Polychromatic	Continuous	1
[6]	Paper	Yellowing	Xenon arc	Monochromatic	Continuous	1
[6]	Paper	Yellowing	Xenon arc	Monochromatic	Intermittent	1
[100]	Coating #1	Chemical change	Solar (100)	Polychromatic	Continuous	0.67
[100]	Coating #2	Chemical change	Solar (100)	Polychromatic	Continuous	0.64
[100]	Coating #3	Chemical change	Solar (100)	Polychromatic	Continuous	0.71
[100]	Polyvinyl chloride film	Chemical change	Solar (100)	Polychromatic	Continuous	0.70
[100]	UV-stabilized polycarbonate	Chemical change	Solar (100)	Polychromatic	Continuous	1.09

p-coefficient observation had a value greater than 1, but the remaining *p*-coefficient values that were not designated as reciprocity failure fall in the range between 0.5 and 1.0.

1.7. Reciprocity law for all materials

Fig. 9 provides a graphical compendium of the *p*-coefficients for all 223 observations. Surprisingly, the *p*-coefficient distribution for the photodegradation of materials (Fig. 8) closely approximates the *p*-coefficient distribution for the combined data set (Fig. 9). In the majority of the observations, specifically, 62%, the reciprocity law was obeyed, while 85% of *p*-coefficient values fall in the range of 0.5–1.0. Of the remaining 15%, 13% of the ob-

servations were designated as reciprocity failure and, as such, the *p*-coefficient values were not computed, while the remaining 2% of the observations had a *p*-coefficient value either less than 0.5 or greater than 1.0.

In addition to the *p*-coefficient values, the reciprocity law literature also provides several noteworthy differences in practice among the different disciplines. These differences include:

- (1) The mercury arc lamp is the most frequently cited light source in the medical, biological and materials photodegradation disciplines; while the most frequently cited light sources in the photographic and photoconducance industries are high-energy or extremely high-intensity sources such as X-ray, gamma ray, and lasers.

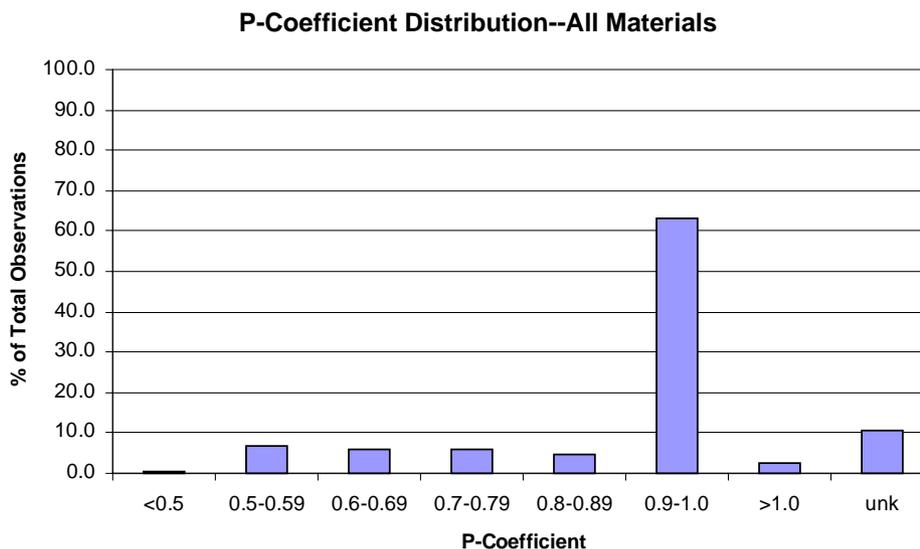


Fig. 9. Distribution of Schwarzschild p -coefficients for all materials. The category 'unk' indicates that reciprocity failure was observed, but the p -coefficient was not computed.

The materials photodegradation community is the highest user of xenon arc lamps. The carbon arc is the least used commercially important light source in reciprocity law experiments.

- (2) The highest radiant flux factor over which the reciprocity law was tested was eight orders of magnitude, i.e., 10^8 [36]. High radiant flux factor experiments were most often employed in the photographic, biological, and medical fields; whereas the smallest number radiant flux factor experiments was conducted in the photodegradation of materials.
- (3) Testing of the reciprocity law using monochromatic light, as opposed to polychromatic light, occurred most often in the medical and biological fields. Polychromatic light was more commonly used in photoconductance and photographic studies than were monochromatic light sources. Only one citation [6] was found in the materials photodegradation literature in which monochromatic light sources were employed to validate the reciprocity law.
- (4) In all the disciplines reviewed, the majority of the experiments used continuous light exposures as opposed to intermittent light. The photographic, biological, and medical disciplines were the most likely to conduct intermittent light exposure experiments; while flash photolysis experiments were the least common mode of exposure and were only performed in the medical, biological, and materials fields.

2. Model

Prior to presenting a model for explaining photolytic activity in all materials, it would be worthwhile to enumerate

various experimental phenomena that any proposed model must be able to explain. These include the following:

1. The Schwarzschild p -coefficient values in photoresponse vs. radiant flux experiments most commonly fall between 0.5 and 1. A Schwarzschild p -coefficient of 0.5 indicates a hole–electron [156] or, equivalently, free radical recombination process; whereas a p -coefficient of 1.0 indicates that the reciprocity law is strictly obeyed. How can Schwarzschild p -coefficient values between 0.5 and 1 arise?
2. The p -coefficient values for the same generic material or for different batches of the same material often have different p -coefficient values (see, for example, Fowler [62]). How can differences in the p -coefficient values be explained?
3. For some materials (see Fig. 10), the p -coefficient value changes markedly from a value between 0.9 and 1.0 at low radiant fluxes to a value between 0.5 and 0.6 at high radiant fluxes [53,66,160,182]. How can a discontinuity in the p -coefficient value with radiant flux be explained?
4. Field exposure environments are more closely mimicked by intermittent exposures than they are by continuous exposures. Are photolytic processes involved in intermittent and continuous laboratory exposures different?
5. The photodegradation response of materials often changes with a change in spectral wavelength, temperature, and moisture content? Can the proposed model account for these changes?

One model that appears to be capable of explaining all of cited experimental phenomena is the *band theory model* (also known as the quantum theory, the solid state theory or, in photography, the Gurney–Mott principle model). The band theory model describes the photophysical events

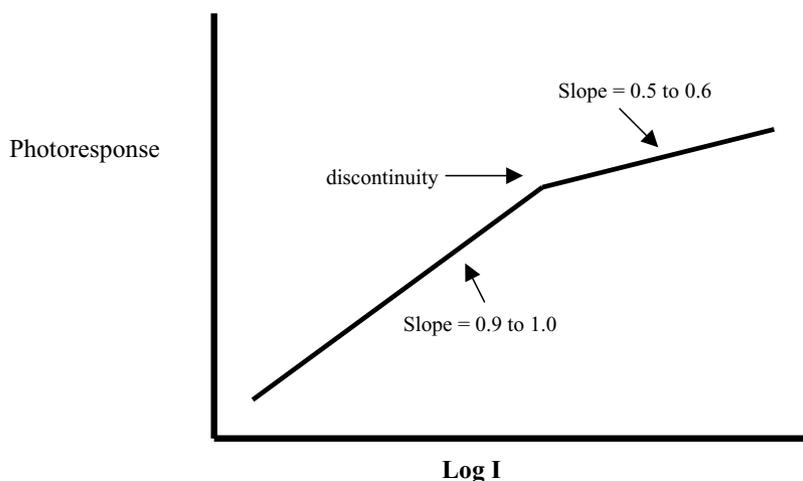


Fig. 10. Photoresponse vs. radiant flux curve exhibiting a discontinuity in the Schwarzchild p -coefficient with radiant flux.

occurring prior to the photochemical events. As pointed out by Gutmann and Lyons [76, Chapter 5], this model is consistent with and complements the optical molecular excitation and transfer model commonly cited in photochemistry texts (see, for example, [150, p. 2]). This model is generally accepted and has been extensively applied in explaining the photoresponse for a wide range of materials and processes including photosynthesis [7,175,101], biochemical processes [29], electrophotographic printing [4,21,50], fluorescence [137], human vision [78,157,158,201], photography [75,125], photocatalytic oxidation [20] and photovoltaic cells [12]. This model has also been widely applied in determining the photostability of dyes and pigments, such as zinc oxide and titanium dioxide, and in explaining photoconductance of long-chained polymeric materials [33,77].

The application of this model to the photodegradation of polymeric materials is supported by the biological and medical photoresponse data cited in Tables 2 and 3. Evidence of photoconductance of long-chain polymeric materials exposed to UV radiation is supported in the literature [77, Chapters 16 and 18; 176]. Linkage between photoconductance and photochemical events has been demonstrated by Herrmann et al. [88] who observed a high correlation between photoconductance and the photocatalytic oxidation of isobutane to acetone in the presence of TiO_2 ; while Mitchell [131] claims that photoconductance behavior has been highly correlated with the sensitivity of photographic emulsions. Published applications of this model to the photodegradation of commercial polymeric materials, however, have not been found. Instead, almost all studies have emphasized photochemical events in explaining all of the observed experimental phenomena. Thus, at this time, the degree to which the band theory model can be applied in describing photodegradation events is uncertain. What is certain is that the application of this model and the application of photoconductance measurements to the photodegradation of polymeric materials should complement, but never supplant, photochemical explanations and photochemical mea-

surements and, in the process, may provide new conceptual, theoretical, and experimental insight into photodegradation research.

According to the band theory model [76], the atoms in a solid are so closely packed that they do not act independently. Instead, they act as an array of coupled resonators (see Fig. 11). As such, the energy states in the outer-shell electrons are changed from local atomic states centered about individual nuclei to states that belong energetically and spatially to the solid as a whole. The effect of this interaction is that the energy states tend to cluster into nearly continuous groups of allowed, discrete energy levels called *energy bands* that are separated by non-allowed energy levels. The highest filled band of electrons is called the valence band, while the lowest unfilled or empty band is called the conduction band. The gap between the top of the valence band and the bottom of the conduction band is called the energy gap (also known as the band gap or the forbidden zone). Obviously, the magnitude of the energy gap is higher for insulators than it is for semiconductors, but otherwise the same photophysical processes apply. Electrons can only be excited into the conduction band if an absorbed photon has sufficient photonic energy to allow the electrons to jump the energy gap leaving a positive hole in the valence band. Once in the conduction band, however, these electrons are free to contribute to the photoconductance and the photodegradation responses for a material; that is, all excited electrons have an equal probability of causing a photochemical change regardless as to whether excitation into the conduction band was caused by UV radiation, ionizing radiation, or X-rays [76,124].

If an applied electric field is superimposed onto a material, then the electrons and holes will migrate in the direction of the field through a process called *photoconduction*. The magnitude of photoconductance is affected by several variables including the mobility of the free carriers (holes or electrons), the lifetime of the free carriers, the number, distribution and cross-sectional size of the traps (see Fig. 12),

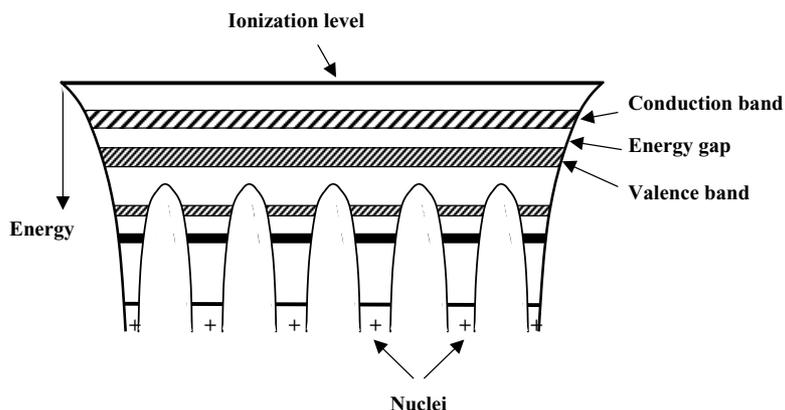


Fig. 11. Band theory schematic displaying the energy bands (taken from [76]).

the location of the Fermi level, and by a number of extrinsic factors such as temperature and relative humidity. The *Fermi level* provides information on the probability that a trapped electron can be thermally excited back into the conduction band [77]. The farther away the Fermi level is from the conduction band (correspondingly the closer it is to the valence band), the greater the amount of thermal energy required and thus the lower the probability of thermally re-exciting a trapped electron into the conduction band. The lifetime of a free carrier is the time until a free carrier is either trapped or undergoes hole–electron recombination. *Traps* reduce the mobility of an excited carrier. In polymeric materials, traps are typically attributed to crystal lattice imperfections, foreign impurities, defective long-range ordering of amorphous and semi-crystalline molecules, chain folds, and structural defects in a polymer chain [77,80,122]. The densities of traps in even highly pure materials can be large in compar-

ison to the number of free electrons in the conduction band (trap densities are often on the order of 10^{15} cm^{-3} while free electron densities in semi-conducting materials are on the order of 10^8 cm^{-3}). It is these differences in trap densities that may explain the high variability in the photoresponse of nominally identical specimens.

Rose [155,156] and Fowler [62] theoretically analyzed the effects of trap distribution and the location of the Fermi level on the Schwarzschild *p*-coefficient. Their analyses appear to be consistent with experimental observations. When traps are absent or at very low concentrations compared with the number of free carriers, the excited electrons decay via hole–electron recombination and the *p*-coefficient will be 0.5. When traps are present, excited electrons located above the Fermi level will have a *p*-coefficient of 0.5 while electrons trapped below the Fermi level will have a *p*-coefficient of 1.0. Thus the *p*-coefficient values for materials will normally fall between 0.5 and 1.0 depending on the distribution of traps and the position of the Fermi level. For example, a material having a uniform distribution of traps will have a *p*-coefficient close to 1.0, while a material having an exponential distribution of traps will have a *p*-coefficient in the range from 0.7 to 0.9.

As radiant flux is increased, a discontinuity in the *p*-coefficient value can occur as follows. Assume a semiconductor material has a uniform distribution of traps. At low enough radiant flux levels, the *p*-coefficient should have a value of 1 (see [155]). As the radiant flux increases, however, more electrons are excited into the conduction band and, thus, more of the traps become filled. As the radiant flux increases, the proportion of filled traps increases until a flux is reached above which all of the traps are filled. Once the traps are filled, the material essentially becomes trap-free and, at this radiant flux, the *p*-coefficient precipitously changes from 1.0 to 0.5 signifying hole–electron recombination. Experimentally, this explanation is consistent with the experimental results of Egerton et al. [53,66,160,182]. Practically, this experimental protocol is commonly used in the electronics industry to estimate the trap density in a material [85,155].

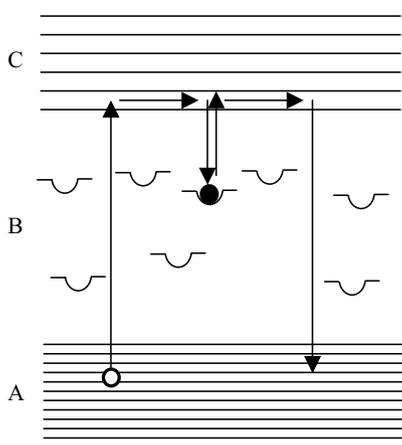


Fig. 12. Schematic showing the electron excitation, electron trapping and hole–electron recombination, where A is the valence band, B the energy gap, and C the conduction band. The squiggle marks in the energy gap indicate traps. The solid circle indicates a trapped electron that can be thermally excited back into the conduction band. Here, the thermally re-excited electron recombines with a hole and in the process liberates heat: in other cases the re-excited electron could cause some type of photochemical damage to the molecule.

The linkage between intermittent and continuous exposure experiments has been most thoroughly studied in photography and photoconductance. From these studies, it was concluded that once a light source is turned off, no more electrons are promoted into the conduction band so the photoelectric signal begins to rapidly decay. The decay process involves the recombination of holes and electrons, electrons falling into traps, and photochemical degradation processes. Intermittent experiments differ from continuous exposure experiments, therefore, in that the photoconductance (and presumably photodegradation) rapidly decays as soon as the light source is turned off and, once the light source is turned back on, it takes a short rise time until the photoresponse again returns to a quasi-equilibrium level. Thus, it is not surprising that the rule-of-thumb in the photographic community is that the photoresponse resulting from intermittent exposures is always less than or equal to that resulting from an equivalent continuous exposure [1,192]. It has also been determined that a critical on-off light frequency exists above which the intermittent and continuous photoresponses are essentially identical [11,140,169,186]. From these observations, the photographic community has concluded that intermittent exposures are a subset of continuous exposures and that the band theory model can be used in explaining the results from both exposure regimes (see [125]).

The effects of temperature, spectral wavelength, moisture and voltage on photoconductance and, thus, on the band theory model, have been primarily investigated in the photography and the photoconductance literatures. No studies were found in the photodegradation literature. Increases in exposure temperature increase both the efficiency of the electron excitation process and electron mobility processes according to the Arrhenius law (see, for example, [56,62,65,97,155,160,168,187,188]). Spectral wavelength effects have mainly been studied in photography [15,185]. The effect of moisture on excitation efficiency and electron mobility has only been investigated in a few cases. Gutmann and Lyons [76, p. 472] claimed that moisture content affects photoconductivity of biological materials by a factor of 10^8 or more; a claim that is supported by the experimental results reported by Murphy and Walker [135]. Numerous studies have investigated the effects of a change in voltage on the photoconductance response of materials [97,126,156,160]. From these studies, they have concluded that photocurrents in materials obey Ohm's law up to several thousand volts and it has been generally been accepted that "photoconductive gain (i.e., the number of electrons passing through a photoconductor per excitation or absorbed photon) can be made infinitely large either by increasing the voltage or by decreasing the electrode spacing" [156, p. 6].

The band theory model appears to offer an explanation for most, if not all, of the experimental phenomena. This conclusion does not denigrate the importance of photochemical processes, but, instead, supports our belief that photophysical processes should be further explored.

3. Summary

Accelerating the photodegradation and weathering of commercial polymers used in both terrestrial and extra-terrestrial applications is of great practical interest. One method of accelerating weathering is by irradiating materials at a high radiant flux and extrapolating the results back to in-service flux levels; such experiments are called reciprocity law experiments. The photographic, biological, medical, and photoconductance communities have studied high radiant flux experiments for a long time and the literature from these disciplines along with that for polymeric material photodegradation have been reviewed. From this review it is concluded that the Schwarzschild law, a power law generalization of the reciprocity law, appears to model adequately the photoresponse of a wide range of materials as a function of radiant intensity. In the overwhelming majority (specifically, 97%) of the 223 cases reviewed and in which the Schwarzschild p -coefficient value was computed, the p -coefficient values fell between 0.5 and 1.0.

In the process of reviewing the literature, a number of experimental phenomena common to all of the materials reviewed were noted and a model capable of explaining these phenomena proffered. The proffered model is a photophysical model having a basis in band theory. This model has been extensively applied and used in explaining the experimental phenomena for all of the reviewed materials except for the photodegradation of polymeric materials. The band theory model provides a photophysical explanation for Schwarzschild p -coefficient values ranging between 0.5 and 1.0 and the other observed phenomena. Implicit in its application is that photophysical processes like photon absorption, electron excitation, and free carrier (excited electrons and holes) migration are basically the same for all materials. Support for the application of the band theory model to the photodegradation of materials is garnered from the knowledge that long-chained polymeric materials are known to photoconduct when exposed to UV radiation and that a linkage has been found between photochemical and photoconductance responses for the few materials in which photoconductance studies have been performed. For example, Herrmann et al. [88] found a high correlation between photoconductance measurements and the photocatalytic oxidation of isobutane to acetone in the presence of titanium dioxide; while Mitchell [131] has indicated that photoconductance measurements are strongly linked to photographic sensitivity. At this time the degree to which the band theory model can be applied in describing photodegradation events is uncertain due to the paucity of photoconductance/photodegradation experimental evidence. What is more certain is that the application of the band theory model to the photodegradation of polymeric materials should complement, but never supplant, photochemical explanations and photochemical measurements. In the process, it is hoped that the application of this model will also provide new conceptual,

theoretical, and experimental insight into photodegradation research.

Acceptance and application of high radiant flux laboratory experiments in materials degradation will be greatly impeded by the paucity of fundamental knowledge regarding the effects of spectral UV radiation, temperature, moisture, and applied voltage, on the reciprocity law or, more likely, the Schwarzschild law. A few citations in the photoconductance and photographic literature on these effects have been found, but only one citation was found in the photodegradation literature in which the effect of wavelength on photoresponse over a wide flux range was examined. Reconciliation and acceptance of the band theory model by itself and in combination with the more generally accepted optical molecular excitation and transfer model used in explaining photochemical phenomena will require extensive experimentation. Specifically, it is not currently clear how the band theory model can be modified, or even if it has to be modified, to take into account photochemical changes occurring in the polymer.

3.1. Future research needs

From this review, exposures of a polymeric material to UV radiation fluxes that are higher than normal and the successful extrapolation of high radiant flux results to in-service radiation flux levels appear to be feasible and, as such, high radiant flux exposures may be a practical strategy for accelerating polymer photodegradation. Implementation of such a strategy, however, will be hindered by the unavailability of commercial high radiant flux exposure equipment and, more importantly, unanswered questions related to the effect of temperature and relative humidity on the photodegradation of polymeric materials at high flux levels.

Development of high radiant flux exposure devices cannot easily be achieved by moving a specimen closer to a high-intensity arc source or by increasing a light source's radiant flux. Such strategies would greatly increase the temperature of a specimen and would probably result in spatially non-uniform iso-irradiance patterns over a specimen's exposed surface. One solution is the use of an exposure device based on integrating sphere technology. Integrating spheres ensure that the flux will be spatially uniform. Moreover, this light source projected into the integrating sphere can easily be equipped with dichroic mirrors to remove thermal load induced by high wattage lamps [119].

Assessing whether unnatural photochemistry is being introduced in photodegrading a specific polymer exposed to a high radiant flux over a range of temperatures and relative humidities should be realizable through the use of well thought-out experimental designs and controlled experiments. Confidently extending conclusions from one polymeric material to all members of a class of polymeric materials or to all polymeric materials and systems is more problematic due to the diversity of polymers that can be produced. Resolution of this dilemma will come about through

improved fundamental understanding of effects that high radiant fluxes have on the photophysical and photochemistry of polymeric materials.

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